Local microenvironment modulation of Pt^0/Pt^{2+} nano-clusters inducing synchronous mass transfer effect to boost catalytic ozonation

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ABSTRACT

Rational catalyst structure design is expected to solve the low O_3 utilization and poor molecular mass transfer efficiency in heterogeneous catalytic ozonation (HCO). Herein, Pt/CMK-3 catalyst with confined space to enhance mass transfer was synthesized and employed for CH_3SH removal. Unlike fully free diffusion in 0–2.0 wt % Pt/CMK-3 and bulk phase diffusion in 10.0 wt% Pt/CMK-3, removal efficiency of 5.0 wt% Pt/CMK-3 was significantly improved to 97.0%, which was attributed to the effective interfacial diffusion of O_3 and CH_3SH through local microenvironment modulation of Pt^0/Pt^{2+} nanoclusters (NCs) inducing synchronous mass transfer. Experimental and DFT calculations confirmed the strong electronic interactions between O_3 and Pt^0 facilitated charge redistribution and preferential O_3 activation. AIMD simulation demonstrated that the synchronous difference in mean-square displacements (MSD) and diffusion coefficient (Dc) of CH_3SH (Dc=0.022) and O_3 (Dc=0.0046) in the confined Pt/CMK-3 system could facilitate CH_3SH migrate to Pt^{2+} through interfacial diffusion. Especially, the d-orbital electrons of Pt NCs interact sequentially with p-orbital electrons of CH_3SH and O_3 to maintain redox of Pt^0/Pt^{2+}. This study provides novel insights on effective mass transfer and kinetic properties of gaseous reaction between oxidant and pollutant by constructing unique interfacial diffusion behaviors.

1. Introduction

Sulfur-containing volatile organic compounds (S-VOCs) emitted into atmosphere are one of the most important potential precursor gaseous pollutants contributing to formation of ozone (O_3), photochemical smog, and urban haze etc. [1,2]. Specially, the ambient concentration limit for methyl mercaptan (CH_3SH, a typical S-VOCs odor gas) is 0.002 mg/m^3, which is much stricter than the concentration limit of H_2S (0.02 mg/m^3) and C_2H_6S (0.02 mg/m^3) [3]. Therefore, the harmless treatment of S-VOCs has attracted extensive attention of the scientific community.

Currently, heterogeneous catalytic ozonation (HCO) technology can effectively remove CH_3SH at room temperature or under complex environment conditions [4–6]. Nonetheless, the accumulation of sulfur-containing intermediates on the surface of metal-containing catalysts lead to catalyst deactivation. And the byproducts may compete with O_3 for adsorption, hindering the efficient utilization of O_3 and

resulting in slow mass transfer in practical applications [7]. How to improve the utilization efficiency of O_3 while ensuring the effective removal of CH_3SH has become one of the challenges in HCO technology.

The effective mass transfer of O_3 and CH_3SH has great potential in promoting the kinetics of catalytic reactions. It can be imagined that the diffusion of O_3 and CH_3SH at the catalyst surface/interface will lead to mass transfer differences [8], and the ideal effective mass transfer determined by characterization can maximize the utilization of O_3 to generate large number of reactive oxygen species (ROSs) [9,10]. In contrast, if the mass transfer and diffusion of O_3 and CH_3SH are quite ineffective, this will result in the quenching of ROSs generated by O_3 (due to the lifespan of ROSs typically being a few picoseconds) [11,12], and ultimately lead to lower catalytic activity as well as catalyst reduction of catalyst active sites. However, it is currently unclear whether the effective mass transfer implies simultaneous diffusion of O_3 and CH_3SH to the active reaction site at the same time, or whether O_3 and CH_3SH sequentially and synchronously diffuse to different active

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site. In this case, by designing an appropriate active metal anchored to the support matrix with confined space, and modulating their local microenvironments to control the regulation of molecular diffusion behavior, it could achieving O_3 activation and highly effective CH_3SH removal in confined space [13].

Recently, ordered mesoporous carbon nanotubes (OM-CNTs) are widely concerned due to their stable chemical properties, special channel structure, large specific surface area and good dispersion of metal catalysts [14]. Therefore, the combination of Pt nanoclusters (NCs) with OM-CNTs can efficiently control the local microenvironment of the catalytic reaction, leading to an enhancement in the local electron density surrounding the metal atoms and influencing the electron filling of the e_g orbitals. This is crucial for both the thermodynamic and kinetic aspects of the surface reaction [15]. Furthermore, the Pt-C interfacial layers presented in the confined meso-channels of OM-CNTs provides a free-moving channel for the inward O_3 and CH_3SH [16]. Predictably, OM-CNTs could effectively improve the activity and durability of metal-based catalysts used as protective shells, and provide confined space for promoting charge/mass transfer for generate more ROSs [15].

Herein, a novel Pt/CMK-3 model catalyst with confined channel was synthesized by coupling EMSI and confined effect between Pt NCs and CMK-3 for removal CH_3SH. Due to the existence of different valence states of Pt (i.e., Pt^0 and Pt^{2+}) in Pt NCs, Pt^0 can effectively activate O_3, while Pt^{2+} is more conducive to the adsorption of CH_3SH. The activation mechanism of O_3 and the degradation pathway of CH_3SH during HCO process were revealed by in-situ Raman, in-situ DRIFTS, and PTR-TOF-MS analysis. DFT calculations and AIMD simulations were used to gain a deeper insight on the electronic interactions between O_3, CH_3SH and catalysts as well as the mass transfer behavior. This work will pave the way for the rational design of catalysts in confinement systems for environmental applications by constructing a confined interfacial diffusive behavior for effective mass transfer between oxidants and S-VOCs molecules.

2. Experimental details

2.1. Preparation of catalysts

Synthesis of Pt/CMK-3: 3.32 mL $H_2PtCl_6 \cdot 6 H_2O$ (4 mg mL^{-1}) was added into 60 mL deionized water and stirred 0.5 h. Then, 100 mg CMK-3 was added to the mixed solution and followed by continuous stirring for 12 h at ambient temperature. After that, excess of NaBH$_4$ (0.1 M) was added to the solution, and reduced for 3 h under ice bath, then washed with a large amount of deionized water. Finally, the solid powder was dried at 60 °C for 8 h. The obtained material denoted as Pt/CMK-3. For comparison, the preparation of Pt/C-Si only changes the substrate material to C-Si, and the rest of the preparation process is the same as above.

More detailed information was provided in **Text S2**.

2.2. Catalytic ozonation removal of CH_3SH

The removal of CH_3SH was measured in a continuous-flow cylindrical stainless steel microreactor (i.d. width = 8 mm; length = 490 mm) with 30.0 mg of catalyst under ambient temperature and atmospheric pressure (**Scheme S1**). CH_3SH concentrations were detected by the CH_3SH sensor (Detcon, DM-400IS), and the inlet CH_3SH concentration was kept 50 ppm. The total flow rate of feed gas was controlled at 100 mL min^{-1} using the mass flow controllers (HORIBA METRON), corresponding to gas hourly space velocity (GHSV) equal to 200,000 mL h^{-1} g^{-1}. The CH_3SH removal rate (η) was calculated as follows [7]:

$$\eta(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \tag{1}$$

Where C_t, C_0 are the concentrations of CH_3SH in the outlet and feeding streams.

2.3. Ab initio molecular dynamics (AIMD) simulations

AIMD simulations were performed using the LAMMPS software. The simulation details were provided in **Text S7**.

3. Results and discussion

3.1. Characterization of catalysts

Pt/CMK-3 was prepared by impregnation reduction method (Fig. 1a). CMK-3 exhibited a uniform mesoporous structure (Fig. S1) and Pt NCs were uniformly embedded in the striated channels of CMK-3 (Fig. 1b) with a mean diameter of approximately 3.5 nm and no observable aggregation (Fig. S2a), the lattice spacing was about 0.215 nm (Fig. 1c), corresponding to the (111) facet of Pt^0 [17]. In contrast, Pt NCs loaded on Pt/C-Si formed large size about 5.7 nm (Fig. S2b) due to the larger surface energy for agglomeration (Fig. 1d), and the lattice spacing of Pt (111) was expanded to 0.229 nm (Fig. 1e). The morphology of CMK-3 and Pt/CMK-3 were observed using scanning electron microscopy (SEM) (Fig. S3a, b). Energy dispersive spectrometer (EDS) spectra illustrated the uniform dispersion of Pt, C, and O elements in Pt/CMK-3 (Fig. S3 c-f). The isotherm of C-Si and Pt/C-Si suggested a non-porous structure (Fig. S4a, b). In contrast, the isotherm of CMK-3 and Pt/CMK-3 exhibited a hysteresis loop, indicating type IV isotherms with mesoporous pore structures [18]. The presence of hysteresis loops indicated the formation of numerous mesoporous structures on the CMK-3 surface after HF etching, which was beneficial to the diffusion and adsorption of molecules. Moreover, Pt/CMK-3 had a larger specific surface (660.7 m^2 g^{-1}) area and more evenly dispersed mesopore than Pt/C-Si (8.4 m^2 g^{-1}) (Table S1). The construction of Pt/CMK-3 confined system leads to the occurrence of Knudsen diffusion at suitable concentrations of CH_3SH and O_3, which enhances the mass transfer process and improves the catalytic activity [19].

The phase composition of synergized catalysts was investigated by X-ray diffraction (XRD) patterns. CMK-3, C-Si, Pt/CMK-3 and Pt/C-Si had a broad diffraction peak around 23.5° and 43.7°, respectively, corresponding to the stacking of the (002) tubular structure plane and in-plane ordering of (101) facet of graphite carbon [20] (Fig. S5a). In addition, after loading Pt NCs, new diffraction peaks appeared at 39.8°, 46.2° and 67.8° (Fig. S5b), corresponding to the (111), (200) and (220) facet of metal Pt (PDF No. 04–0802) [21]. Furthermore, the model of Pt NCs was established and the fitted XRD pattern was consistent with standard card (Fig. S6). The strongest diffraction peak of (002) obviously shifted to lower angle, indicating that Pt NCs were successfully introduced into the channel of CMK-3. According to Sabatier theory [22], the confinement effect of CMK-3 can effectively prevent the agglomeration of metal during the reduction deposition process, but tend to nucleate and grow slowly and uniformly, which is beneficial to the more sufficient dispersion of metals, exposing more active sites, and ultimately promoting long-term catalytic reaction.

The surface functional groups were analyzed by Fourier transform infrared spectroscopy (FTIR). As depicted in Fig. S7a, the C-O stretching vibration peak at 1248 cm^{-1} of Pt/CMK-3 had a slight blue shift compared with CMK-3, which was attributed to the EMSI effect between Pt NCs and CMK-3. C-Si substrate and Pt/C-Si have obvious diffraction peaks at 1138 cm^{-1}, 958 cm^{-1} and 815 cm^{-1}, which corresponded to Si-O-Si stretching vibration, Si-OH stretching vibration and Si-O symmetric stretching vibration of silicon oxide materials. However, after loading Pt NCs, the infrared characteristic peaks of Pt/C-Si did not shift (Fig. S7b) as the characteristic peak of Pt/CMK-3, indicating a weak interaction between Pt NCs and C-Si substrate, which is not conducive to the uniform dispersion of Pt NCs. Raman spectra (Fig. S8a, b) displayed that the
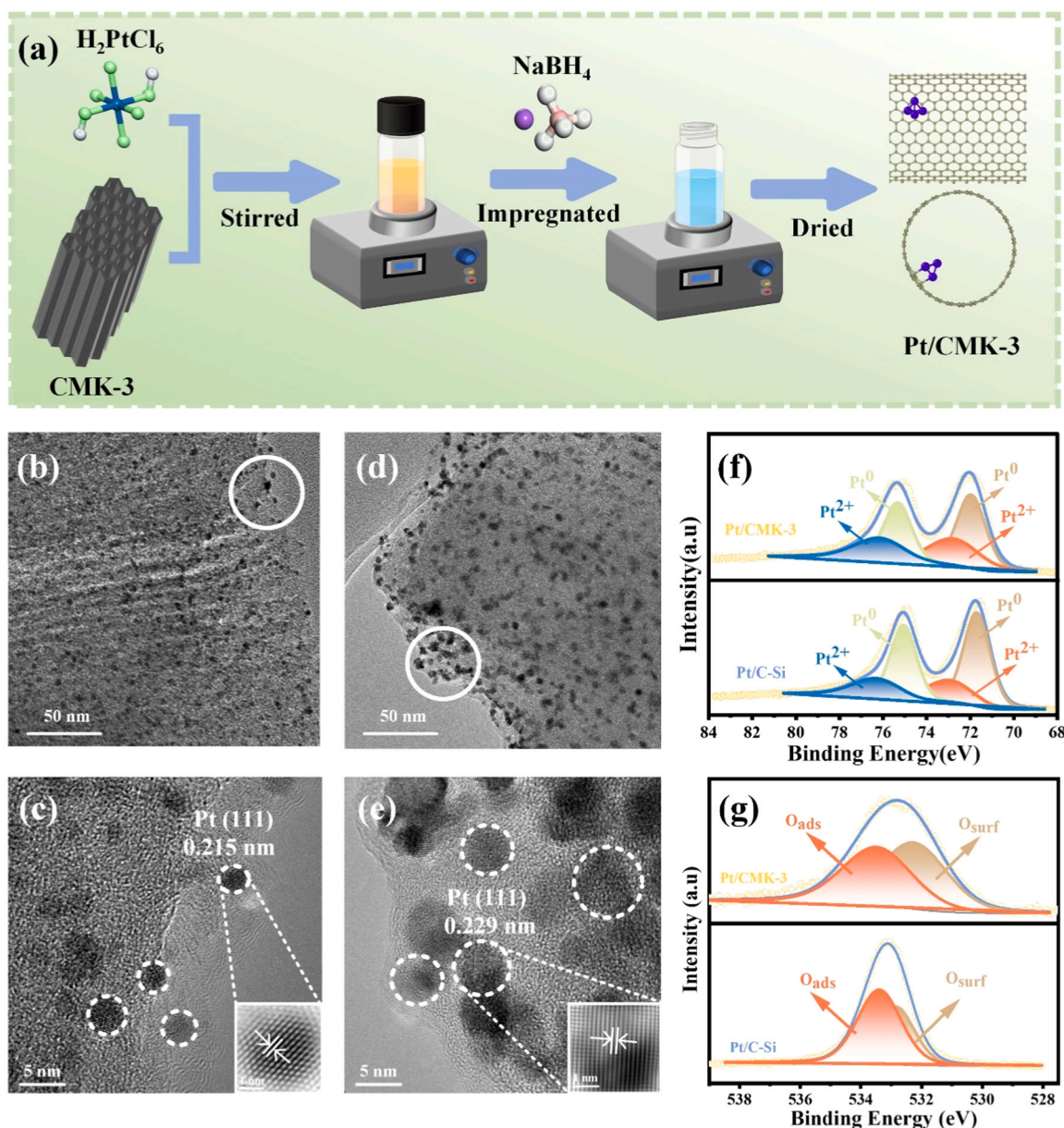
Fig. 1. (a) Schematic diagram of Pt/CMK-3 synthesis process; (b) TEM and (c) HR-TEM images of Pt/CMK-3; (d) TEM and (e) HR-TEM images of Pt/C-Si; XPS spectra of (f) Pt 4 f, and (g) O 1 s for Pt/CMK-3 and Pt/C-Si.

peaks at around 1340 cm^{-1}, designated as the D-band, are associated with the disordered carbon structure; the peaks at approximately 1585 cm^{-1}, assigned to the G-band, are related to the in-plane vibration of sp^2 bonded carbon [23]. And the I_D/I_G value was 1.20 and 1.19 for CMK-3 and C-Si substrate, respectively, confirming that CMK-3 possessed more surface defects. However, after loading Pt NCs, the defect degree of both Pt/CMK-3 (I_D/I_G = 1.15) and Pt/C-Si (I_D/I_G = 1.14) showed a decreasing tendency. Low-temperature electron paramagnetic resonance (EPR) profiles also confirmed that CMK-3 had more surface defects, whereas Pt/C-Si and Pt/CMK-3 have almost no detectable peaks present (Fig. S9), suggesting that Pt NCs deposited at the surface defect sites of the substrate, and enhanced the interaction between Pt NCs and substrate [24].

The chemical composition and surface value states of catalysts were analyzed by X-ray photoelectron spectroscopy (XPS). The survey spectrum showed that Pt has a weak peak strength in Pt/CMK-3 (Fig. S10a), which may be caused by Pt NCs encapsulated in the pore and/or channel of CMK-3. The C 1 s peak was no significant shift, exhibiting the same

chemical state in Pt/CMK −3 and Pt/C-Si (Fig. S10b). In Fig. 1f, the high-resolution of Pt 4 f can be divided into four peaks at 71.95, 72.80, 75.33, and 76.15 eV, corresponding to Pt 4 $f_{7/2}$ and Pt 4 $f_{5/2}$ orbitals of Pt^0 and Pt^{2+} [25], respectively. The binding energy of Pt^0 in Pt/CMK-3 was increased by 0.31 eV compared with that in Pt/C-Si, indicating a strong EMSI between Pt NCs and CMK-3. The actual Pt content was quantitatively determined by ICP-OES (Table S2) and showed similar loading of Pt in Pt/CMK-3 (4.41 wt%) and Pt/C-Si (4.01 wt%). The content of Pt^{2+} in Pt/CMK-3 was 35.1%, while in Pt/C-Si was only 29.1%. This is due to the smaller size promoted better dispersion of Pt NCs on Pt/CMK-3 and led to a higher Pt^{2+} content, which it more conducive to the effective utilization of electrons in Pt^{2+}/Pt^0 redox cycle. The high-resolution of O 1 s could be divided into two peaks at 532.2 eV and 533.4 eV (Fig. 1g), belonging to adsorbed oxygen (O$_{ads}$: •O^{2-} and •OH species) and surface residual water (H$_2$O$_{surf.}$). The presence of more reactive oxygen-containing groups on CMK-3 (Table S3) facilitates to reduce the energy barrier for activation of adsorbed O-oxygen species to generate ROSs.

The reducibility and the amount of oxygen vacancies (O_v) of Pt/CMK-3 and Pt/C-Si were measured by H_2-temperature-programmed reduction (H_2-TPR). There were three reduction peaks on Pt/CMK-3, and the two Gaussian-shape reduction peaks at 272 °C and 382 °C were the hydrogen consumption reduction peaks of Pt^{2+} to Pt^0 species (Fig. S11a) [26]. Pt/CMK-3 displayed a lower temperature of the reduction peak (272 °C) than Pt/C-Si (367 °C), indicating that the coupling effect of EMSI and confinement effect significantly enhanced the metal reduction ability [27]. Generally, excellent low-temperature reducibility promotes the oxygen mobility and facilitates the adsorption-activation cycle of oxygen species [28]. Furthermore, cyclic voltammetry (CV) test was further used to analyze the redox ability of

catalysts (Fig. S11b). As is well known, O_3 has a strong affinity for electrons and is easy to gain electrons to generate ROSs [4]. When O_3 was saturated in the electrolyte solution, the oxidation peak located near 1.0 eV of Pt/CMK-3 and CMK-3 was significantly enhanced, indicating a strong electronic interaction between O_3 and Pt NCs.

To further investigate the dispersibility, valence states and local atomic coordination structures of Pt NCs in Pt/C-Si and Pt/CMK-3, X-ray absorption near-edge structure (XANES) and extended X-ray fine structure (EXAFS) spectra were conducted. In Fig. 2a, the white line intensities of Pt/C-Si and Pt/CMK-3 were located between the comparison materials (Pt foil, $PtCl_4$, PtO_2), and the intensity of Pt/CMK-3 was slightly higher than that of Pt/C-Si, indicating that Pt in Pt/CMK-3 has a
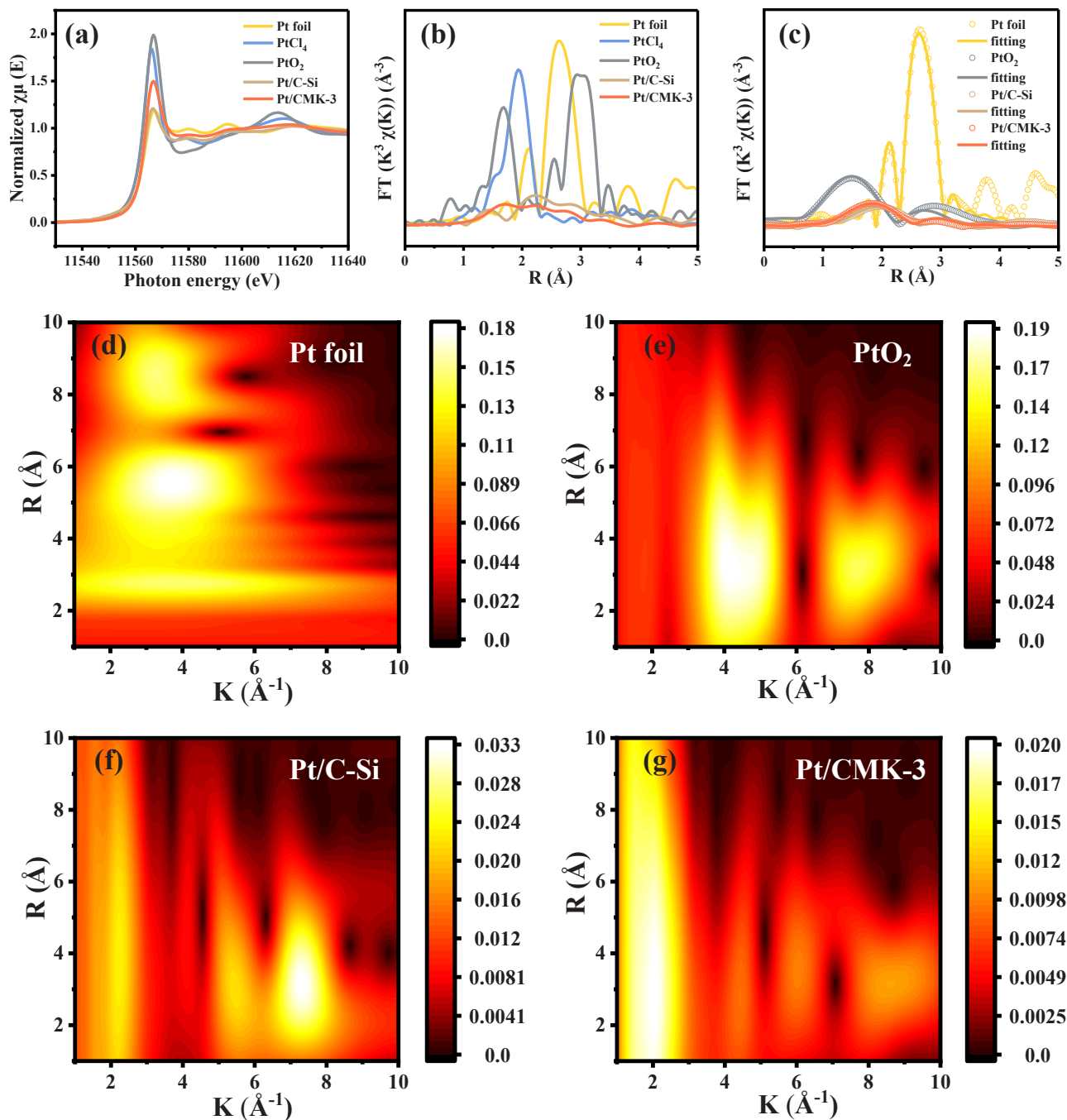

Fig. 2. (a) Pt L3-edge XANES spectra of Pt foil, $PtCl_4$, PtO_2, Pt/C-Si and Pt/CMK-3; (b) k^3-weighted Pt L3-edge Fourier-transformed EXAFS spectra of Pt foil, $PtCl_4$, PtO_2, Pt/C-Si and Pt/CMK-3; (c) Pt L3-edge EXAFS fitting results of Pt foil, PtO_2, Pt/C-Si and Pt/CMK-3 in R space; (d) - (g) Wavelet transforms of k^3-weighted EXAFS for Pt foil, PtO_2, Pt/C-Si and Pt/CMK-3.

higher oxidation state (such as Pt^{2+}) and a lower coordination number compared with PtO_2, resulting in stronger interactions between Pt NCs and CMK-3 [29]. Fig. 2b displayed the R-space of Pt L3-edge in Pt/C-Si and Pt/CMK-3. The peak at 2.6 Å corresponded to Pt-Pt scattering, the peak at 1.6 Å was attributed to Pt-O bond and the peak at 1.95 Å was related to Pt-Cl bond [30]. The profiles of the weaker peak located around 1.5 Å (higher than Pt-O bond) in Pt/C-Si corresponded to Pt-C bond, indicating the interaction between Pt NCs and substrate through Pt-C coordination. It is noteworthy that a secondary peak can be also observed at 2.10 Å in both Pt/C-Si and Pt/CMK-3, but it does not exist in PtO_2 and $PtCl_4$, implying a coupling effect between Pt-metal atoms except for Pt-C bonding. Moreover, the wavelet transforms (WT) analysis further confirmed the existence of Pt sites (Fig. 2d-g, Fig. S12). Compared with the control samples, the WT-EXAFS of Pt/C-Si and Pt/CMK-3 only displayed the main maximum intensity value between k ≈ 2.0 Å^{-1} and R ≈ 1.0–6.0 Å^{-1} were assigned to the Pt-C distance of the first neighbor shell. The higher WT intensity in Pt/CMK-3 suggested a stronger EMSI between Pt and CMK-3 [31]. The EXAFS fitting spectra of Pt foil, PtO_2, Pt/C-Si and Pt/CMK-3 were performed to probe quantitative atomic structure of Pt sites (Fig. 2c and Table S4). The coordination number of Pt was about 4.69 in Pt/C-Si, and the corresponding bond length was about 2.00 ± 0.08 Å. Whereas the coordination number of Pt in Pt/CMK-3 was about 1.81, and the corresponding bond length in R space was 1.96 ± 0.05 Å. The low-coordination structure facilitates the breaking of the centrosymmetric structure with higher electron cloud density metal centers and lower reaction energy barriers [32]. According to crystal field theory, the adsorption capacity between small molecules and catalyst is essentially a linear binding between the intermediate and the catalyst atomic orbitals [33]. Thus, the magnitude of the coordination number between Pt and C was closely related to the electron filling of d orbitals of Pt. The lower the coordination number of Pt in Pt/CMK-3, the more d electrons were filled in antibonding orbitals, thus effectively regulating the adsorption of the molecule. Whereas higher Pt^{2+} content in Pt/CMK-3 also revealed a more suitable adsorption capacity than Pt/C-Si, which is not too strong (with a higher Pt^0 content) nor too weak (with a higher Pt^{2+} content).

3.2. Performance of CH_3SH removal

In Fig. 3a, CH_3SH removal performance of C-Si and CMK-3 were 52.0% and 70.0%, and Pt/CMK-3 reached 97.0%, exceeding the state-of-the-art findings (Table S5). In contrast, the performance of Pt/C-Si first increased to 88.0% and gradually decreased to 80.0% after 1 h. This may be due to insufficient Pt^{2+} sites, making it difficult to adsorb CH_3SH [34]. Therefore, the relationship between the number of active sites (reflected by Pt loading) and the catalytic performance was further explored. When the theoretical loading of Pt NCs was 2.0 wt%, the removal efficiency was only 76.0%. In contrast, the performance was significantly enhanced to 97.0% when Pt NCs loading increased to 5.0 wt%. Notably, further increasing Pt loading to 10.0 wt%, CH_3SH removal efficiency decreased to 90.0% (Fig. 3b). This was attributed to the strong interactions between Pt atoms tend to induce the aggregation of Pt NCs to form nanoparticles (NPs) (Fig. S13a-f) according to Ostwald ripening theoretical [35,36]. The average size rapidly increases to 27.0 nm when Pt loading reached 10.0 wt% (Fig. S14a-b), and the CH_3SH transfer seems to be "blocked" by the large Pt NPs. Herein, three possible pathways for CH_3SH diffusion in Pt/CMK-3 may be proposed: (1) Fully free diffusion when Pt load is between 0 ~ 2.0 wt%; (2) Interfacial diffusion at Pt-C interface when Pt load reaches 5.0 wt%; and (3) Bulk phase diffusion when Pt load reaches 10.0 wt%. As mentioned above, the fully free diffusion of CH_3SH in CMK-3 or 2.0 wt% Pt/CMK-3 was very inefficient due the weak interaction between CH_3SH and the catalyst, and the limited number of active sites for insufficient activation of O_3 [37]. Similarly, as previously revealed in experiments, diffusion through the bulk phase of 10.0 wt% Pt/CMK-3 was difficult due to the large diffusion barrier. Therefore, the interfacial diffusion of CH_3SH in 5.0 wt% Pt/CMK-3 exhibits the highest efficiency and the optimal interaction capacity.
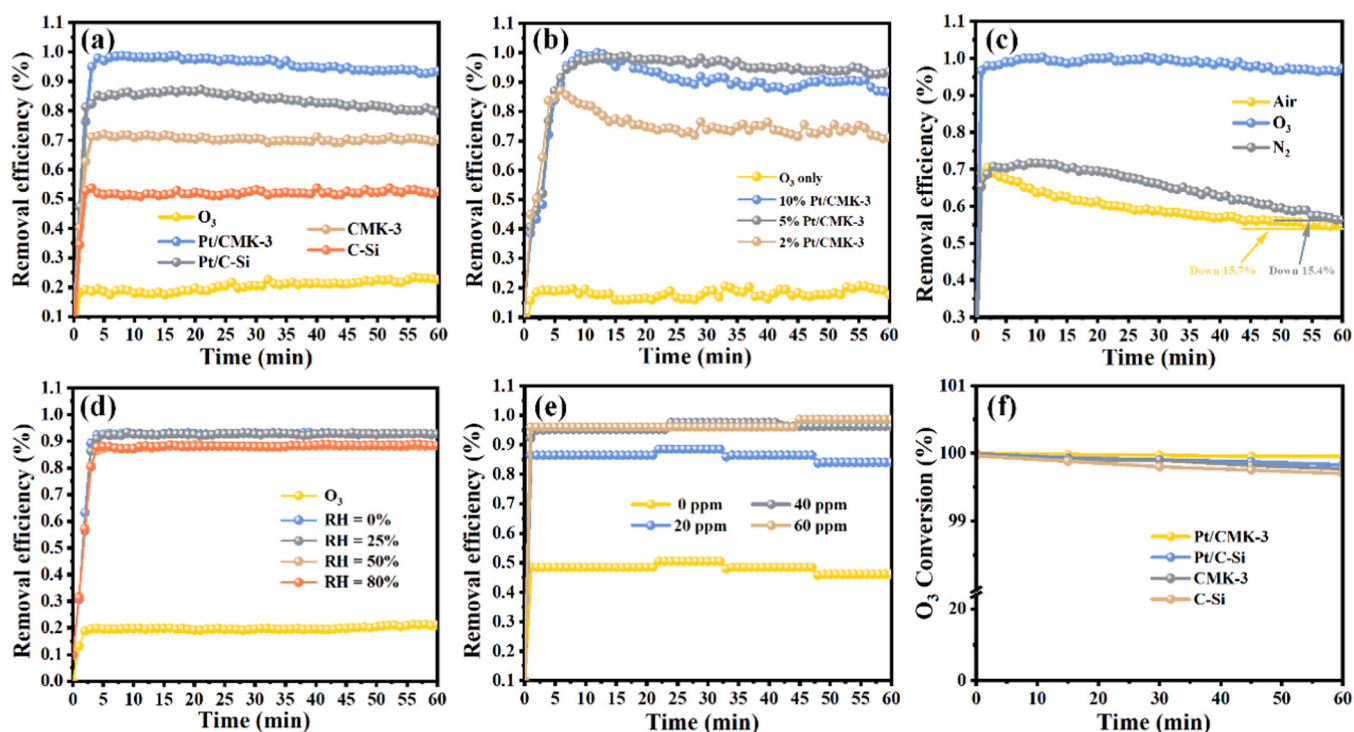

Fig. 3. (a) Catalytic ozonation for CH_3SH removal by Pt/CMK-3, Pt/C-Si, CMK-3, and C-Si; (b) Catalytic ozonation for CH_3SH removal by Pt/CMK-3 with different Pt loading; (c) CH_3SH removal under different atmospheres by Pt/CMK-3 and (d) Effect of humidity on catalytic ozonation for CH_3SH removal by Pt/CMK-3; (e) Effect of O_3 concentration for CH_3SH removal by Pt/CMK-3; (f) O_3 utilization efficiency in different systems. (Reaction conditions: [catalysts mass] = 30.0 mg, [CH_3SH concentration] = 50 ppm, [RH] = 0%, [O_3 concentration] = 40 ppm, [GHSV] = 200,000 mL h^{-1} g^{-1}, and [temperature] = 25 ℃.).

The ability of Pt/CMK-3 to activate O_3 was further verified by the performance study of CH_3SH removal under different atmospheres. In Fig. 3c, Pt/CMK-3 displayed comparable removal efficiency about 62.0% under air and N_2 atmospheres, but the removal efficiency decreased by 15.7% and 15.4% with the time prolonged to 1 h, respectively. The absence of oxidant (O_3) in the air and N_2 atmosphere may explain the challenge in generating ROSs within Pt/CMK-3 system, thereby impeding the efficient removal of CH_3SH and resulting in the accumulation of sulfur-containing intermediates on the catalyst. In contrast, the removal efficiency reached to 97.0% under O_3 atmosphere. This result indicated that O_3 efficiently activated by Pt/CMK-3 and generated large amounts of ROSs through chain reactions. Relative humidity (RH) also has great influence on the catalytic performance in gas-solid catalytic system. The performance of CH_3SH removal kept around 93.0% when RH was 0%, 25%, and 50% (Fig. 3d), which indicated that the presence of moderate amount of H_2O molecules in the system was beneficial to the formation of intermediates oxidation species (*OH/*O), further improved the catalytic performance. When RH increased to 80%, the performance slightly decreased (88.0%), indicating that Pt/CMK-3 has better resistance to moisture [13]. In addition, the effect of O_3 concentration on the catalytic activity was further explored. When the O_3 concentration was 0 ppm, the removal efficiency of CH_3SH was about 52.0%. With the increase of O_3 concentration, the removal efficiency increased significantly and reached 99.5% when the O_3 concentration was 60 ppm (Fig. 3e). These results further demonstrated the important role of O_3 as an oxidant in the removal of CH_3SH. The O_3 concentration at the reactor outlet was monitored to assess the efficiency of O_3 utilization. Fig. 3f illustrated that the O_3 conversion rate of Pt/CMK-3 system was 99.95%, better than other systems. The residual O_3 concentration at the outlet of reactor was below 0.02 ppm, indicating that the high efficiency of O_3 utilization in the catalytic ozonation process by Pt/CMK-3, so as to avoid secondary pollution by the elevated O_3 levels in the exhaust gas.

Furthermore, the performance of CH_3SH removal in confined Pt/ CMK-3 system remained at a satisfactory level (89.5%) after 8 cycles (Fig. S15a). In addition, XRD patterns further proved the structure did not change after long-term reaction. TEM images also revealed no obvious aggregation of Pt NCs, and the size was consistent with the initial state (Fig. S15b-d). These results indicated that CMK-3 can better stabilize Pt NCs, thus ensuring a good physical structure stability and catalytic activity of Pt/CMK-3.

3.3. Analysis of intermediate products

In situ diffuse reflectance infrared Fourier transform spectroscopy (in-situ DRIFTS) was employed to determine the possible intermediate products. In Fig. 4a, the strong bands observed near 2950 cm^{-1}, 950 cm^{-1}, and 810 cm^{-1} corresponded to the stretching vibration of C-H bond, vibration of S-C-H bond, and vibration of C-H bond [38], respectively. The appearance of absorption peaks indicated that CH_3SH was adsorbed on Pt/CMK-3 and partially undergoes conversion to form primary product. Noteworthy, the weaker bands at 1256 cm^{-1} and 1078 cm^{-1} could be attributed to the R-SO_2-R vibration and S=O vibration of SO_3^{2-} [39], which also indicated that some of the adsorbed CH_3S^- was further oxidized to intermediate products or C-S bond broken to formed SO_3^{2-} during the adsorption process. For HCO process (Fig. 4b), the signals of the bands related to oxidation products became stronger, indicating that Pt/CMK-3 more completely oxidized CH_3SH. In detail, the characteristic bands of CH_3SH in the adsorption phase significantly weakened or even disappeared, indicating that the CH_3S^- further oxidized to other products with the involvement of O_3. And the bands associated with ozonated substances (O_3^-) at 780 cm^{-1} and SO_4^{2-} vibrations at 1052 cm^{-1} increased with time going on [40]. In contrast, a series of new bands at 1715 cm^{-1}, 1591 cm^{-1} were assigned to C=O stretching vibrations of -COO and ν(COO-) peaks of HCOOH [41], while the bands at 1379 cm^{-1}, 1204 cm^{-1} were associated with sulfonate $CH_3SO_3^-$ vibrations [42]. The important intermediate species were normalized in adsorption process, and the intensity of chemisorbed
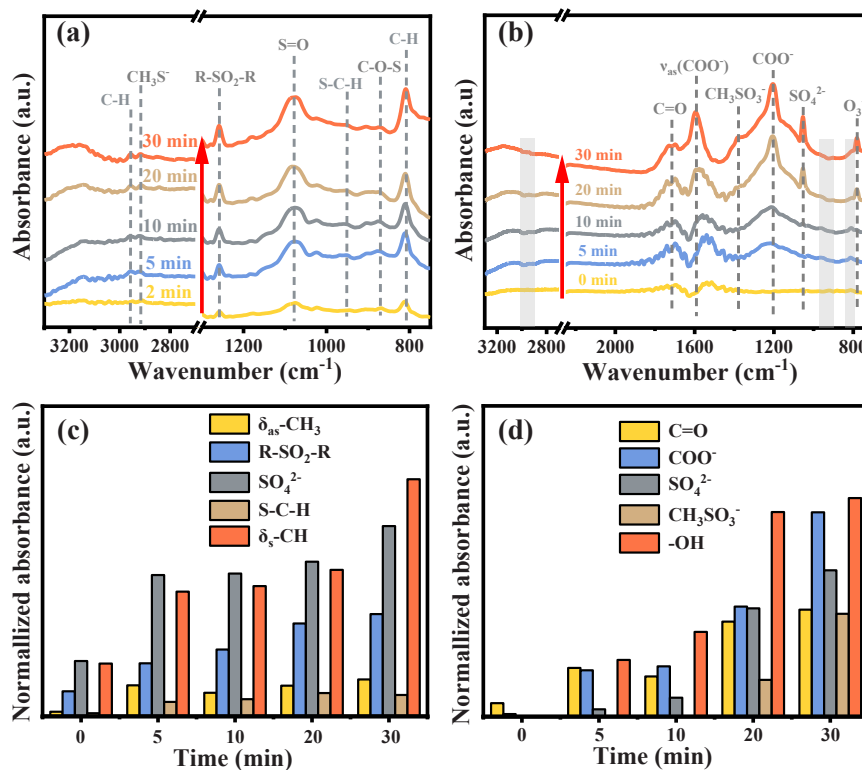

Fig. 4. In-situ DRIFTS spectra of CH_3SH adsorption (a) and catalytic ozonation (b) over Pt/CMK-3; Normalized species evolution of (c) CH_3SH adsorption and (d) catalytic ozonation over Pt/CMK-3.

CH_3SH and SO_4^{2-} grew with adsorption time (Fig. 4c), while the bands of S-C-H and $-CH_3$ (CH_3SSCH_3, CH_3SCH_3) stabilize around 20 min, indicating that CH_3SSCH_3 and CH_3SCH_3 were the main intermediate products of the adsorption process. In addition, CH_3SH was gradually oxidized during the HCO process (Fig. 4d), the intensity of $CH_3SO_3^-$ and SO_4^{2-} intermediates bands increased, while the intensity of the -COO and -OH like product bands fluctuated during the reaction, which was attributed to the final oxidation of HCOOH and C=O to form harmless CO_2 and further escape from Pt/CMK-3. Furthermore, the difference in hydrophobicity between Pt/C-Si and Pt/CMK-3 (Fig. S16) also confirmed the enhanced mass transfer of Pt/CMK-3 to generate more ROSs. The exhaust gas products were determined and analyzed by PTR-TOF-MS, the mass spectra displayed in Fig. S17 and Table S6. Compared with Pt/C-Si system (Fig. S17a), the signal of CH_3SH (m/z=49.01) in the exhaust gas during catalytic ozonation by Pt/CMK-3 was weaker (Fig. S17b). Furthermore, the signals of intermediate products such as CH_3CHO (m/z=45.03) and CH_3SOH (m/z=65.00) in Pt/CMK-3 system were relatively weak, suggesting that the degradation of CH_3SH involves the cleavage of C-S and C-H bonds. This result indicated that Pt/CMK-3 system displayed a more efficient CH_3SH removal, and the final products in outlet were mainly inorganic mineralized CO_2 and SO_4^{2-}.

The oxidation products were further analyzed to compare the activity of Pt/CMK-3 and Pt/C-Si systems (**Fig. S18**). Initially, the CO_2 production in the exhaust gas was assessed and it was shown that CO_2 content in Pt/CMK-3 system was $2.15 * 10^{-5}$ mmol, while minimum CO_2 production in Pt/C-Si system was $5.60 * 10^{-6}$ mmol. Furthermore, the presence of SO_4^{2-} on the catalyst surface was confirmed using IC. After 1 h of reaction, the content of SO_4^{2-} on Pt/CMK-3 surface was $4.39 * 10^{-5}$ mmol, significantly higher than that of Pt/C-S system ($6.56 * 10^{-6}$ mmol), indicating that Pt/CMK-3 system has good oxidation and mineralization of CH_3SH and finally convert it into CO_2 and SO_4^{2-}.

3.4. Investigation of reactive oxygen species (ROSs)

Electron paramagnetic resonance (EPR) experiment was used to ascertain the ROSs generated in HCO process. In Fig. 5a, Pt/CMK-3 detected a clear 1:2:2:1 quadruplet signal of DMPO-•OH [43] and showed higher intensity than that in Pt/C-Si system and sole O_3 condition, indicating that Pt/CMK-3 more easily activating O_3 to generate •OH. In addition, DMPO-•OH gradually increased with the prolonged exposure time to 10 min (Fig. 5d), indicating that •OH was the main ROSs in removal of CH_3SH in Pt/CMK-3 system. The significant signal peaks of DMPO-•O_2^- (1:1:1:1) [44] was observed in confined Pt/CMK-3 system (Fig. 5b), and its signal intensities of •O_2^- radicals were further enhanced with the time extended to 10 min of introduce O_3 in confined Pt/CMK-3 system (Fig. 5e), indicating that O_3 was continuously activated to generate •O_2^- as the main ROS in HCO process. The characteristic signals of TEMP-$^1O_2$ were shown in Fig. 5c and Pt/CMK-3 system had the strongest triple 1:1:1 typical signals [10], while the typical signals gradually increased with time prolonged to 10 min in confined Pt/CMK-3 system (Fig. 5f), which meant the large number of $^1O_2$ was generated. In-situ Raman used to further explore the activation of O_3. Except for the original D and G bands of Pt/CMK-3 system, three new characteristic peaks were observed at 850, 1020 and 1090 cm^{-1} (Fig. S19a, b), corresponding to the adsorbed peroxide species (*O_2), adsorbed atomic oxygen (*O_{ads}) and surface-O_3 [45], respectively. In contrast, under N_2 atmosphere, no significant signal peaks of oxidatively active species were detected in Pt/CMK-3 (Fig. S19c, d), indicating that O_3 was the main electron acceptor and the initial species of free radical chain reaction [46]. From these results, we found that Pt^0 can activated O_3 to *O_2 and *O_{ads} in the confined Pt/CMK-3 system, and *O_{ads} (ORP = 2.43 V) and *O_2 (ORP = 1.35 V) [4] with a certain oxidation capacity can partial oxidation CH_3SH to intermediate products.
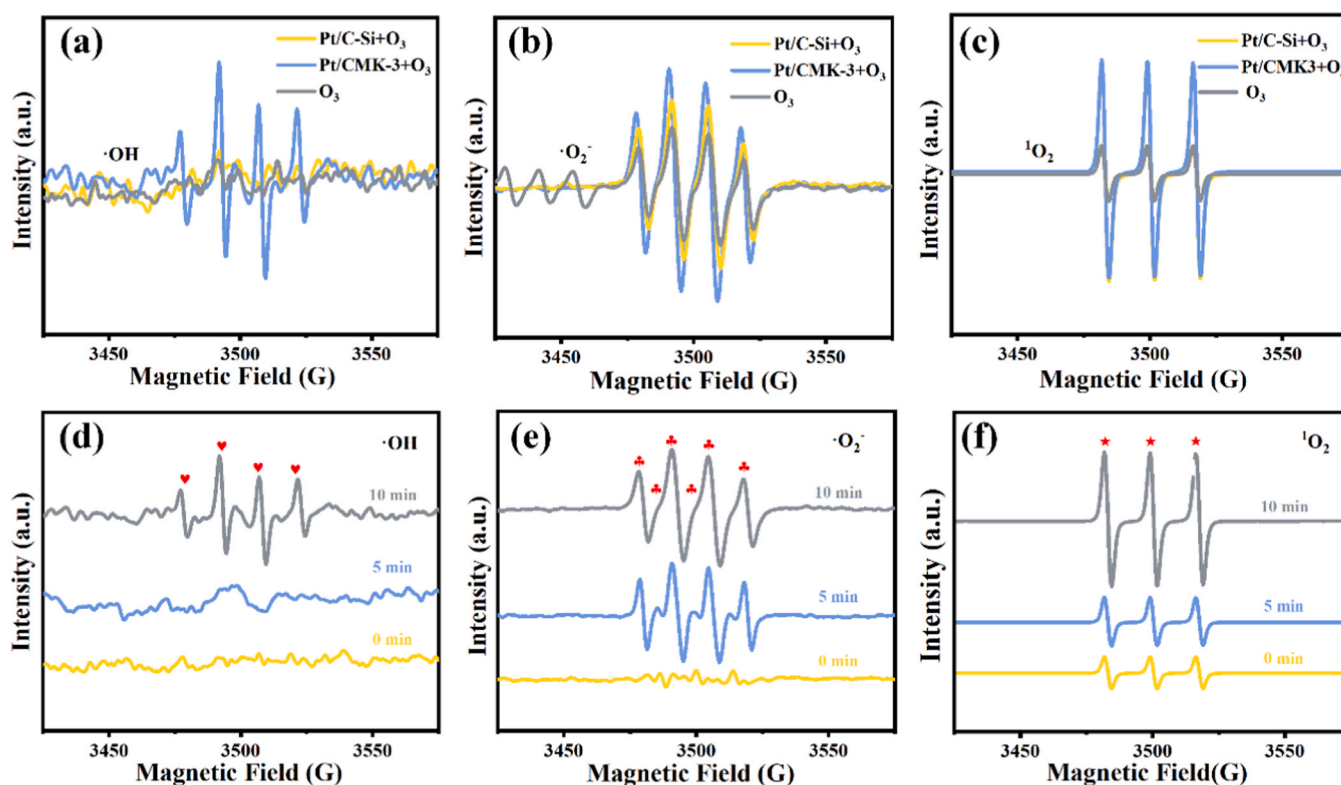

Fig. 5. EPR spectra of (a) DMPO-•OH, (b) TEMP-•O_2^- and (c) DMPO-$^1O_2$ in different systems; EPR spectra of (d) DMPO-•OH, (e) TEMP-•O_2^- and (f) DMPO-$^1O_2$ for catalytic ozonation with Pt/CMK-3 system of different reaction time.

3.5. Reaction Mechanism

The valence states of Pt and relative content situation before and after reactions were explored to further investigative the reaction mechanism (**Fig. S20a, b** and **Table S7**). After catalytic reaction, the content of Pt^0 on Pt/CMK-3 slightly decreased from 64.9% to 60.7%, and the content of Pt^{2+} content slightly increased from 35.1% to 39.3%. The result demonstrated that the electron-rich region of Pt^0 in Pt/CMK-3 transfers electrons to O_3 to generate intermediate oxygen species (*O_2 and *O_{ads}), while the contaminants can act as electron donors to adsorb at the electron-deficient center of the catalyst to maintain the electron gain/loss balance of the catalyst [47]. In addition, after CH_3SH was adsorbed on Pt/CMK-3, the content of Pt^0 increased from 64.9% to 70.2%, indicating that electrons were transferred from CH_3SH to Pt^{2+}, and CH_3SH lost electrons to become $CH_3S\bullet/CH_3SSCH_3$. The catalytic performance was maintained through the electron cycle between Pt, O_3 and CH_3SH, and as well as the continuous activation of O_3 by Pt^0. In contrast, the content of Pt^0 on Pt/C-Si decreased more significantly from

70.9% to 60.6% after reaction, while the Pt^{2+} content increased from 29.1% to 39.4%, which may be ascribed to that partial Pt^0 (loaded outside of C-Si) was easily oxidized to Pt^{2+} by excess H_2O and O_2, and thus the catalytic performance decreased as the reaction proceeded.

DFT calculations were carried out to reveal the catalytic mechanism on molecular level. Subsequently, the theoretical structure model was built and optimized (Fig. S21a, b), the formation energy of Pt/CMK-3 was −5.40 eV, while Pt/C-Si was −2.92 eV. The lower formation energy meant Pt/CMK-3 had better structural stability [48]. Besides, the adsorption energy (E_{ads}) of O_3 and CH_3SH on Pt/CMK-3 and Pt/C-Si (Fig. 6a, b) revealed that the binding strength of O_3 to Pt/CMK-3 (E_{ads} = −3.45 eV) was higher than that of Pt/C-Si (E_{ads} = −2.09 eV). The corresponding bond length of O_1-O_2 stretched from 1.29 Å to 1.94 Å (Table S8), indicating that Pt^0 sites can directly enhanced adsorption/activation of O_3 and facilitates the generation of *O_{ads} and *O_2. In contrast, the O_1-O_2 bond length was only stretched from 1.29 A to 1.81 Å, indicating that Pt/C-Si has little ability to adsorb and activate O_3. Since both O_3 and CH_3SH molecules are present in the system, the
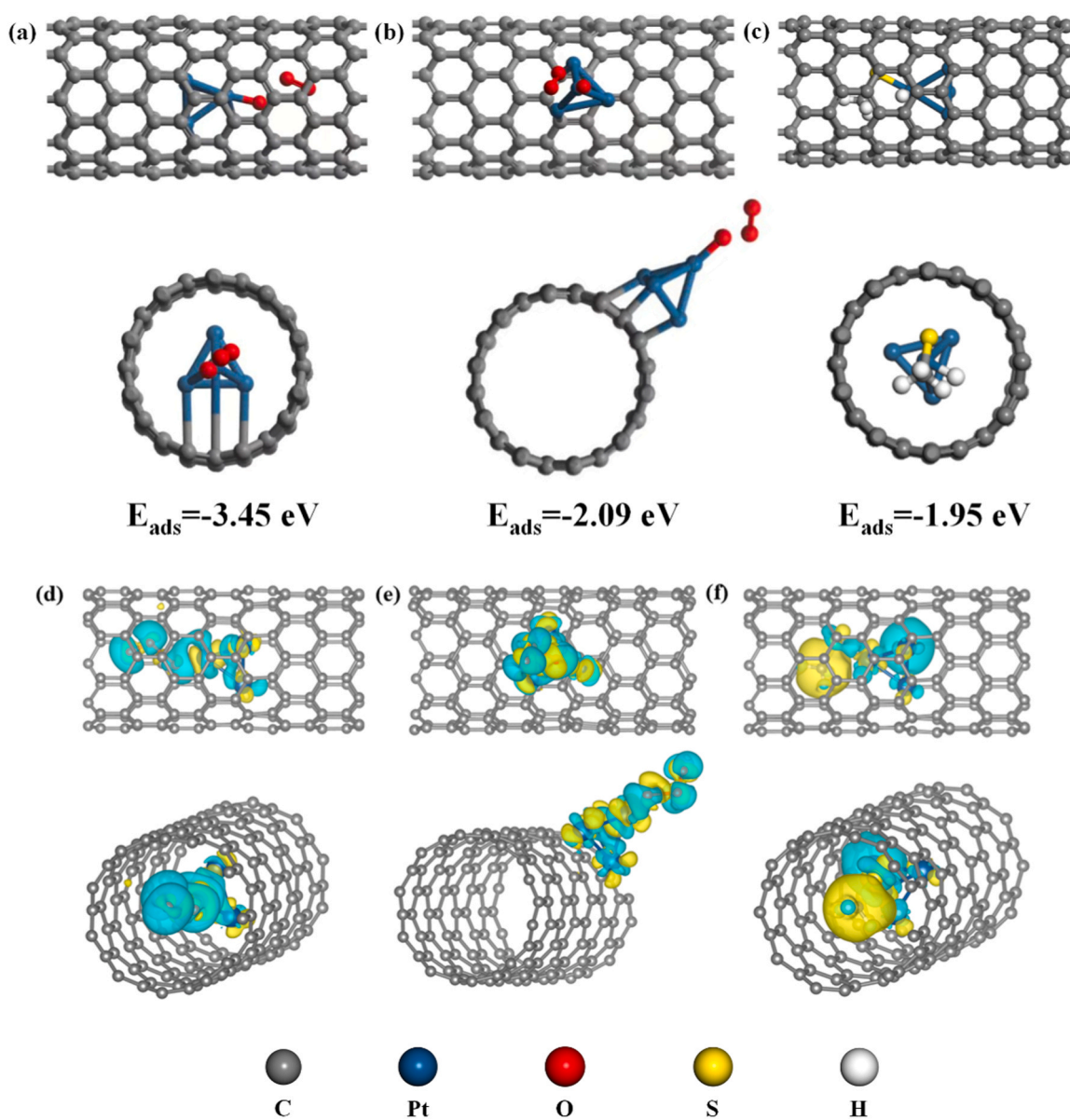

Fig. 6. Adsorption energy of O_3 on (a) Pt/CMK-3 and (b) Pt/C-Si; (c) Adsorption energy of CH_3SH on Pt/CMK-3; Charge density difference (CDD) of (d) Pt/CMK-3, (e) Pt/C-Si after adsorption of O_3 and (f) Charge density difference (CDD) of Pt/CMK-3 adsorption of CH_3SH (Blue region indicates electron accumulation, yellow region indicates electron depletion).

adsorption order and adsorption strength in confined Pt/CMK-3 system need to be further investigated. In Fig. 6c, E_{ads} of CH_3SH on Pt^{2+} sites of Pt/CMK-3 (-1.95 eV) was smaller than that of O_3 on Pt^0 sites of Pt/CMK-3 (-3.45 eV), implying a highly exothermic adsorption process, and meant that O_3 has stronger adsorption ability on Pt/CMK-3, and accept electrons from Pt^0 to generate large number of ROS due to strong electronic interactions. However, the electron interaction between CH_3SH and Pt^{2+} is weaker, tending to donate electrons to generate $CH_3S\bullet/CH_3SSCH_3$, ultimately maintaining the redox cycle of Pt^0/Pt^{2+} [49]. The d-band center (ε_d) was used to semi-quantitatively describe the adsorption strength of CH_3SH (Fig. S22). And ε_d position of Pt decreased from -1.74 eV to -2.10 eV after CH_3SH adsorbed on Pt/CMK-3, which was lower than the change of Pt/C-Si (-1.75 eV to -1.83 eV), this attributed to the d-orbitals of Pt^{2+} gained electrons from CH_3SH, resulting in the further weakening of the binding strength of the CH_3SH molecule. Considering the too strong binding on Pt^{2+} for oxidation, the weaker adsorption energy of Pt/CMK-3 is essential for an enhanced CH_3SH removal efficiency [50]. Charge density difference (CDD) of O_3+Pt/CMK-3 (Fig. 6d) and O_3+Pt/C-Si (Fig. 6e) illustrated the O atoms in O_3 strongly gain electrons from Pt^0 in Pt/CMK-3 [51]. However, the CDD between O_3 and Pt NCs was more heterogeneous in Pt/C-Si system, indicating a weaker electronic interaction between O_3 and Pt/C-Si. The CDD of CH_3SH-Pt/CMK-3 (Fig. 6f) and Bader charge analysis (Fig. S23) illustrated that C and S atoms in CH_3SH lost about 0.25 |e| and 0.08 |e|, the average Pt NCs gained about 0.05 |e|, respectively.
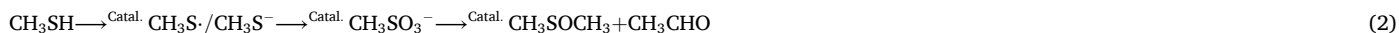
The electrostatic potential results presented the electron distribution of CH_3SH molecule was prone to rearrangement due to the electronegativity difference between the C and S elements, and it was easy to

O_3 and CH_3SH in different systems, compared with O_3+Pt/CMK-3 (MSD = 7.22 $\times 10^{-15}$ m^2 s^{-1}), the average displacement of O_3 is smaller in (O_3+CH_3SH) +Pt/CMK-3 system (MSD = 2.76 $\times 10^{-15}$ m^2 s^{-1}). In addition, the diffusion coefficients (Dc) of O_3 and CH_3SH in confined Pt/CMK-3 system were calculated based on MSD of 1 ns [55]. In Fig. 7d, the Dc of O_3 (0.0046 nm^2 ps^{-1}) was lower than that of CH_3SH (0.022 nm^2 ps^{-1}), which revealed the physical interaction (collision, repulsion, etc.) exists between O_3 and CH_3SH during the diffusion process, this meant that the mass transfer process will be more sequential, and further reduce the energy loss in the mass transfer process and increase the efficiency of mass transfer [56].

Based on ex/in-situ experiments and theoretical calculations, the process of CH_3SH removal in confined Pt/CMK-3 system can be divided into two processes: during adsorption process, the interfacial diffusion triggered by the confinement effect of Pt/CMK-3 significantly enhances the effective mass transfer of O_3 and CH_3SH. This allows CH_3SH and O_3 to diffuse synchronized to the Pt^{2+} sites and Pt^0 sites, and undergo electronic interactions that promote more electron delocalization. The strong chemisorption and electron transfer processes for the d-p orbital hybridization between Pt NCs and CH_3SH oxidized CH_3SH to $CH_3S\bullet/$ CH_3S^-, and further break C-S bond to formed CH_3CHO, CH_3SOCH_3, SO_3^{2-} intermediates; In catalytic ozonation process, the absorbed O_3 in Pt^0 sites was activated to generate oxygenated intermediates (*O_{ads} and *O_2), further transformed into other strong oxidation ROSs ($\bullet OH$, $\bullet O_2^-$, $^1O_2$) and deeply oxidized primary products to SO_4^{2-}, CO_2 and H_2O.

The summarized reaction pathways following:

(1) Adsorption stage

$$CH_3SH \xrightarrow{\text{Catal.}} CH_3S\cdot/CH_3S^- \xrightarrow{\text{Catal.}} CH_3SO_3{}^- \xrightarrow{\text{Catal.}} CH_3SOCH_3 + CH_3CHO \qquad (2)$$
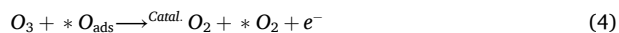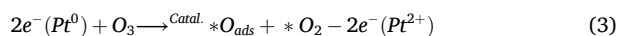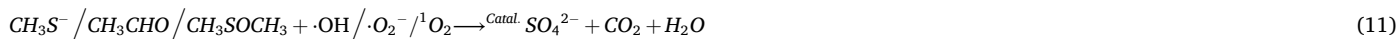
gather charge on the methyl C atom and lose charge on the sulfhydryl S atom, while the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) indicated that CH_3SH molecule loses electron and the ability to lose electron sites (**Fig. S24 a-d**) [52], respectively. In addition, natural population analysis (NPA) charge distribution of CH_3SH and the Fukui index were calculated to quantitatively assess the active sites for pro-site, nucleophilic, and free radical attack [53]. According to Fukui function, when the value of f^+ (or f^-) is higher, the molecule is more susceptible to nucleophilic (or electrophilic) attacks. So, the high Fukui index values of S2 ($f^- = 0.619$ and $f^0 = 0.487$) indicated that it is more susceptible to attack by $\bullet O^{2-}$, $^1O_2$, and $\bullet OH$ to form CH_3S^-, and H6 also has a relatively high Fukui index ($f^+ = 0.349$, $f^0 = 0.240$) indicated that it can also react with e$^-$ species to form $CH_3S\bullet$ (**Fig. S24e**) [54]. Therefore, CH_3SH was more susceptible to electrophilic attack by electrostatic potential analysis, and finally oxidized to SO_4^{2-}, CO_2 and H_2O.

Ab initio molecular dynamics (AIMD) provided a new sight to explored the interfacial diffusion behaviors and molecular dynamics, which was extremely important for in-depth understanding the structure-efficacy relationship. Within a certain simulation time, O_3 mixed CH_3SH moved more disorder in confined Pt/CMK-3 system, while pure O_3 moved in an orderly fashion in O_3+Pt/CMK-3 system (Fig. 7 a1-b3, Fig. S25). Fig. 7c depicted the mean square displacement (MSD) of

(2) The chain reaction of ROS: (* refers to the active site on the catalyst)

$$2e^- (Pt^0) + O_3 \xrightarrow{\text{Catal.}} *O_{ads} + *O_2 - 2e^- (Pt^{2+}) \qquad (3)$$

$$O_3 + *O_{ads} \xrightarrow{\text{Catal.}} O_2 + *O_2 + e^- \qquad (4)$$

$$*O + H_2O \xrightarrow{\text{Catal.}} 2 \cdot OH \qquad (5)$$

$$4 \cdot OH \xrightarrow{\text{Catal.}} {}^1O_2 + 2H_2O \qquad (6)$$

$$*O/*O_2 + e^- \xrightarrow{\text{Catal.}} \cdot O^{2-} \qquad (7)$$

$$\cdot O^{2-} + e^- \xrightarrow{\text{Catal.}} {}^1O_2 \qquad (8)$$

(3) CH_3SH catalytic ozonation stage:

$$Pt^{2+} + 2e^- (CH_3SH) \xrightarrow{\text{Catal.}} Pt^0 + CH_3S\cdot + CH_3S^- \qquad (9)$$

$$2CH_3S\cdot \xrightarrow{\text{Catal.}} CH_3SSCH_3 \qquad (10)$$

$$CH_3S^- \Big/ CH_3CHO \Big/ CH_3SOCH_3 + \cdot OH \Big/ \cdot O_2^- / {}^1O_2 \xrightarrow{\text{Catal.}} SO_4{}^{2-} + CO_2 + H_2O \qquad (11)$$
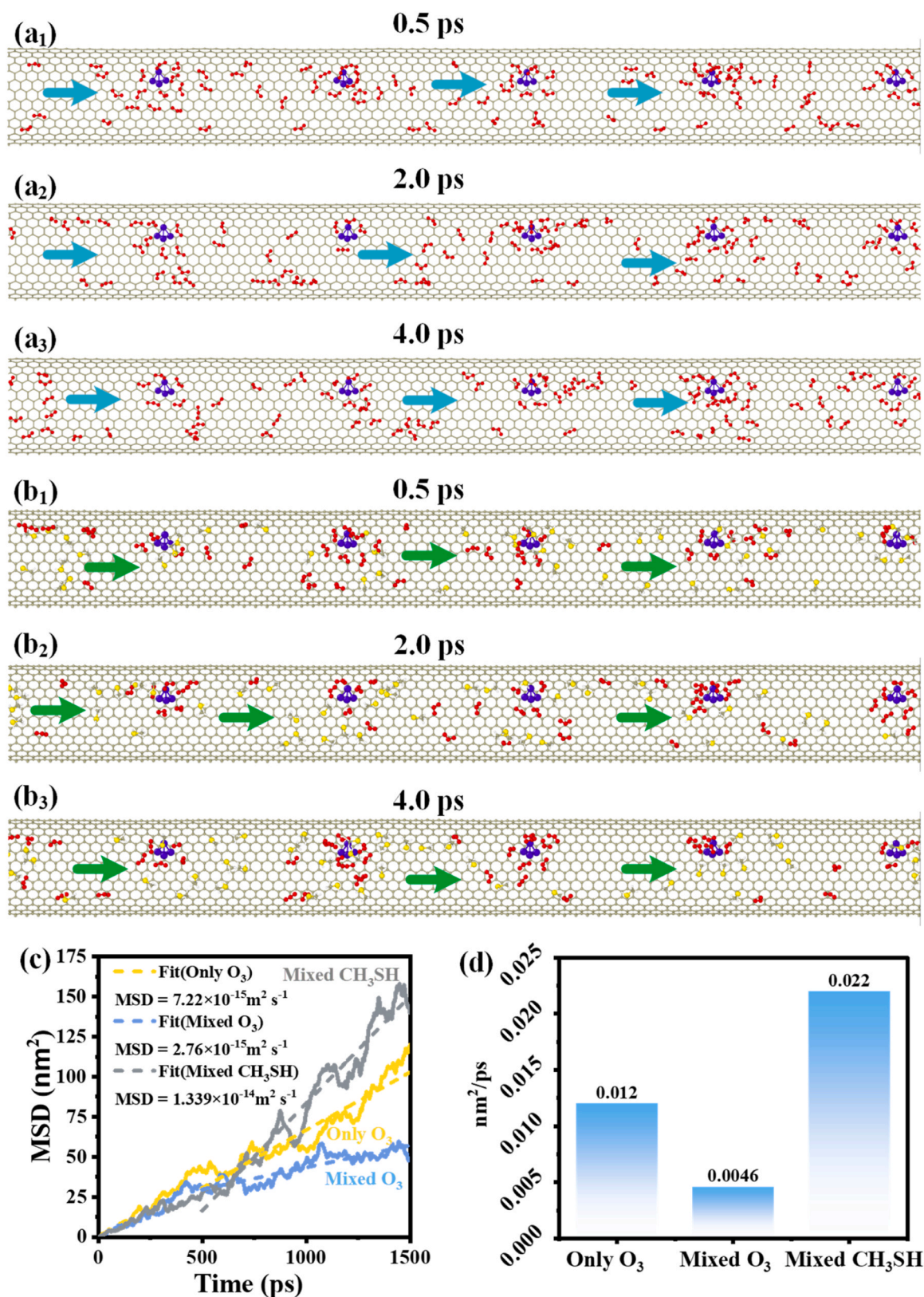
Fig. 7. Typical snapshots of dynamic diffusion changes of O_3 alone at 0.5, 2.0, 4.0 ps (a_1, a_2, a_3) and O_3+CH_3SH on Pt/CMK-3 at 0.5, 2.0, 4.0 ps (b_1, b_2, b_3); The corresponding (c) mean square displacement (MSD) and (d) diffusion coefficients (Dc) of O_3 and CH_3SH vs. AIMD simulation time.

4. Conclusions

This study emphasizes an innovative strategy to effectively remove CH_3SH through local microenvironment modulation of Pt^0/Pt^{2+} NCs inducing synchronous mass transfer. The rational confined structure of catalysts can effectively enhance the mass transfer efficiency of gaseous oxidant molecules (O_3) and gaseous pollutant molecules (CH_3SH). The effective interfacial diffusion of O_3 and CH_3SH at Pt-C interface with appropriate metal loading (5.0% Pt/CMK-3) through synchronous mass transfer, enables O_3 and CH_3SH transfer to Pt^0 and Pt^{2+} sites in the confined Pt/CMK-3 system, respectively, thus leading to the significantly increased removal of CH_3SH. In addition, DFT calculations and AIMD analysis further elucidate the intrinsic mechanism of O_3 activation and CH_3SH elimination. In summary, the study not only opens a new avenue for in-depth investigation on the diffusion mechanisms and kinetic properties of gaseous reaction between oxidant molecules and pollutant molecules at the catalyst surface/interface, but also provides new ideas for rational design of catalyst structure.

CRediT authorship contribution statement

Tao Zhong: Methodology, Validation, Computation, Investigation, Data curation, Writing – original draft, Visualization. **Xianhu Long:** Data curation, Visualization. **Manhui Luo:** Data curation, Visualization. **Su Tang:** Data curation, Formal analysis. **Wenbin Huang:** Data curation, Formal analysis. **Huinan Zhao:** Writing – review & editing, Methodology, Validation, Investigation, Data curation, Software. **Lingling Hu:** Writing – review & editing, Methodology, Validation, Investigation, Data curation, Software. **Shuanghong Tian:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing. **Dong Shu:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing. **Chun He:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124162.

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